

# Lithium Dendrite Prevention for Lithium-Ion Batteries

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Project ID #ES275



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# Overview

## Timeline

- Start date: Oct. 2015
- End date: Sept. 2018
- Percent complete: 70%

## Budget

- Project funding
  - DOE share 100%
- Funding received in FY16: \$400k
- Funding received in FY17: \$340k

## Barriers addressed

- Growth of lithium dendrites
- Low Coulombic efficiency
- Low charge current density

## Partners

- Argonne National Laboratory
- U.S. Army Research Laboratory

# Relevance/Objectives

- Enable lithium (Li) metal to be an effective anode in rechargeable Li-metal batteries using conventional 4-V Li-ion intercalation cathodes for long cycle life at a reasonably high current density.
- Explore various factors that affect the morphology of Li deposition.
- Develop nonaqueous electrolytes and additives to protect Li metal anode and to increase Li Coulombic efficiency (CE).
- Improve the stability and the conductivity of solid electrolyte interphase (SEI) layer on Li metal anode to enable long cyclability.
- Suppress Li dendrite formation on Li-metal anode.



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# Milestones

Date	Milestones	Status
Dec. 2016	Verify the formation of a transient high $\text{Li}^+$ -concentration electrolyte layer during fast discharging by direct microscopic observation	Completed
March 2017	Identify the effects of dual-salt electrolytes on Li metal protection during fast charging	Completed
June 2017	Identify new electrolytes that are stable with both Li and high voltage cathode	On track
Sept. 2017	Further Increase CE of Li cycling in the new electrolyte	On track

# Approach

- Use additives in dual-salt electrolytes to form highly conductive SEI, protect Li metal, enable long cycle life and fast chargeability of Li metal batteries.
- Use in-situ ToF-SIMS to detect if a transient high-concentration electrolyte layer is formed on Li metal anode surface during fast discharge process of Li metal batteries.
- Develop new electrolyte formulations (including salts and additives in carbonate solvent mixtures) to achieve high Li CE and stable with high voltage cathode.

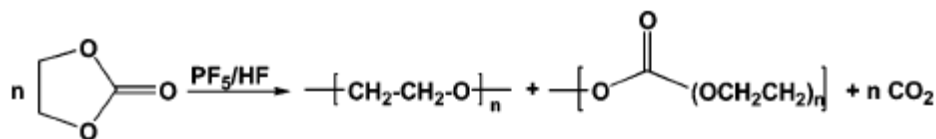


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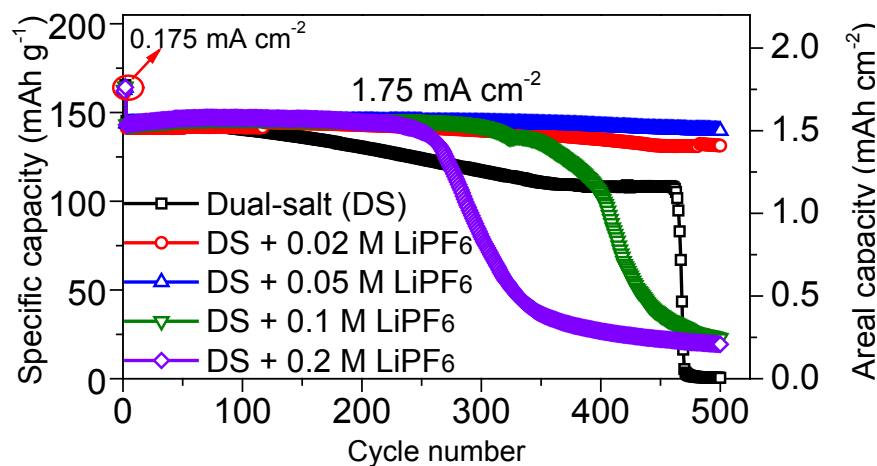
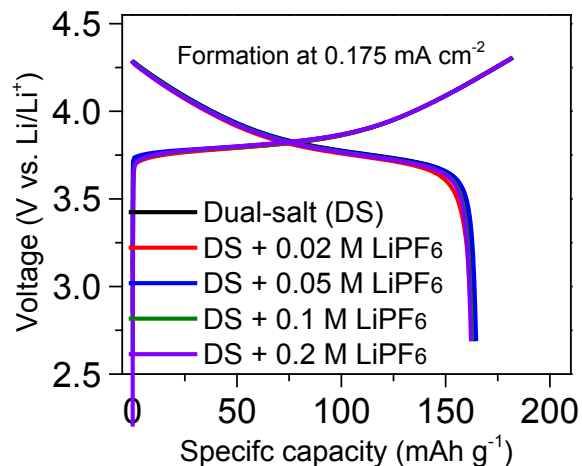
# Technical Accomplishments

## Selection of additive and optimization of LiPF<sub>6</sub> additive amount on Li metal battery performance



K. Xu, *Chem. Rev.*, 2004, **104**, 4303-4417

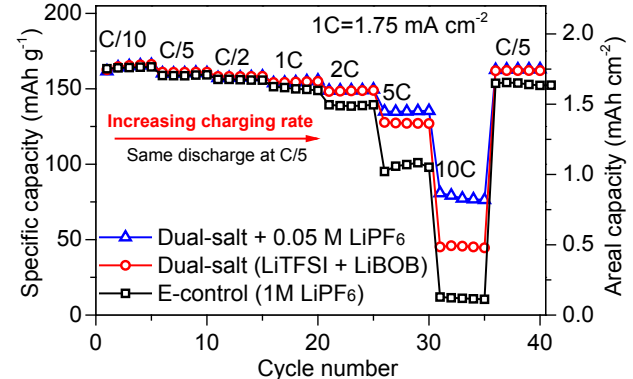
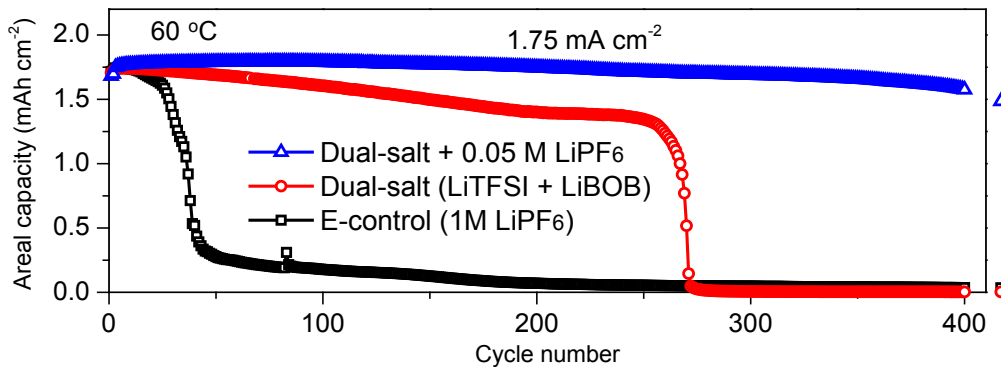
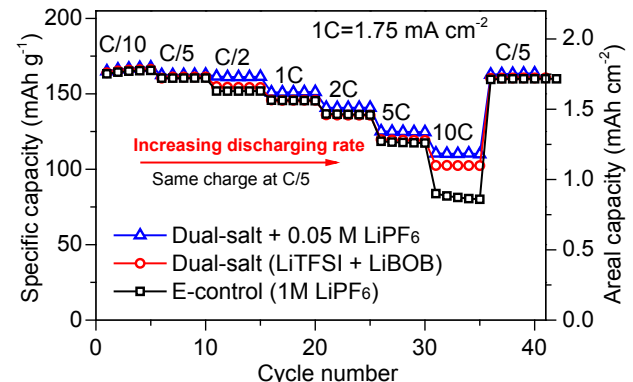
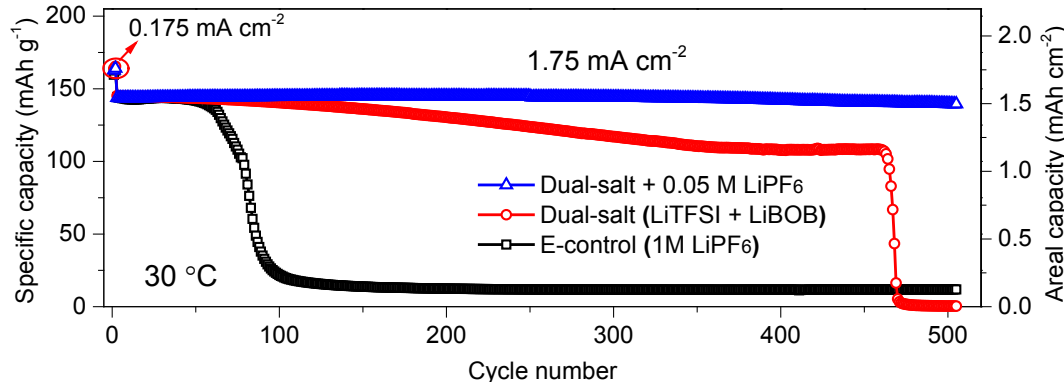
➤ Decomposition products of LiPF<sub>6</sub> additive act as catalysts to initiate the ring-opening polymerization of EC molecules to form polyethers, polycarbonates, etc.



- Li||NMC442 (1.75 mAh cm<sup>-2</sup>), 2.7 ~ 4.3 V
- Dual-salt (DS) electrolyte: 0.6 M LiTFSI + 0.4 M LiBOB in EC-EMC (4:6 by wt.)
- ✓ LiPF<sub>6</sub> additive at the optimum content (0.05 M, i.e. 0.6% by wt.) is the key to achieve enhanced long-term cycling stability.

# Technical Accomplishments

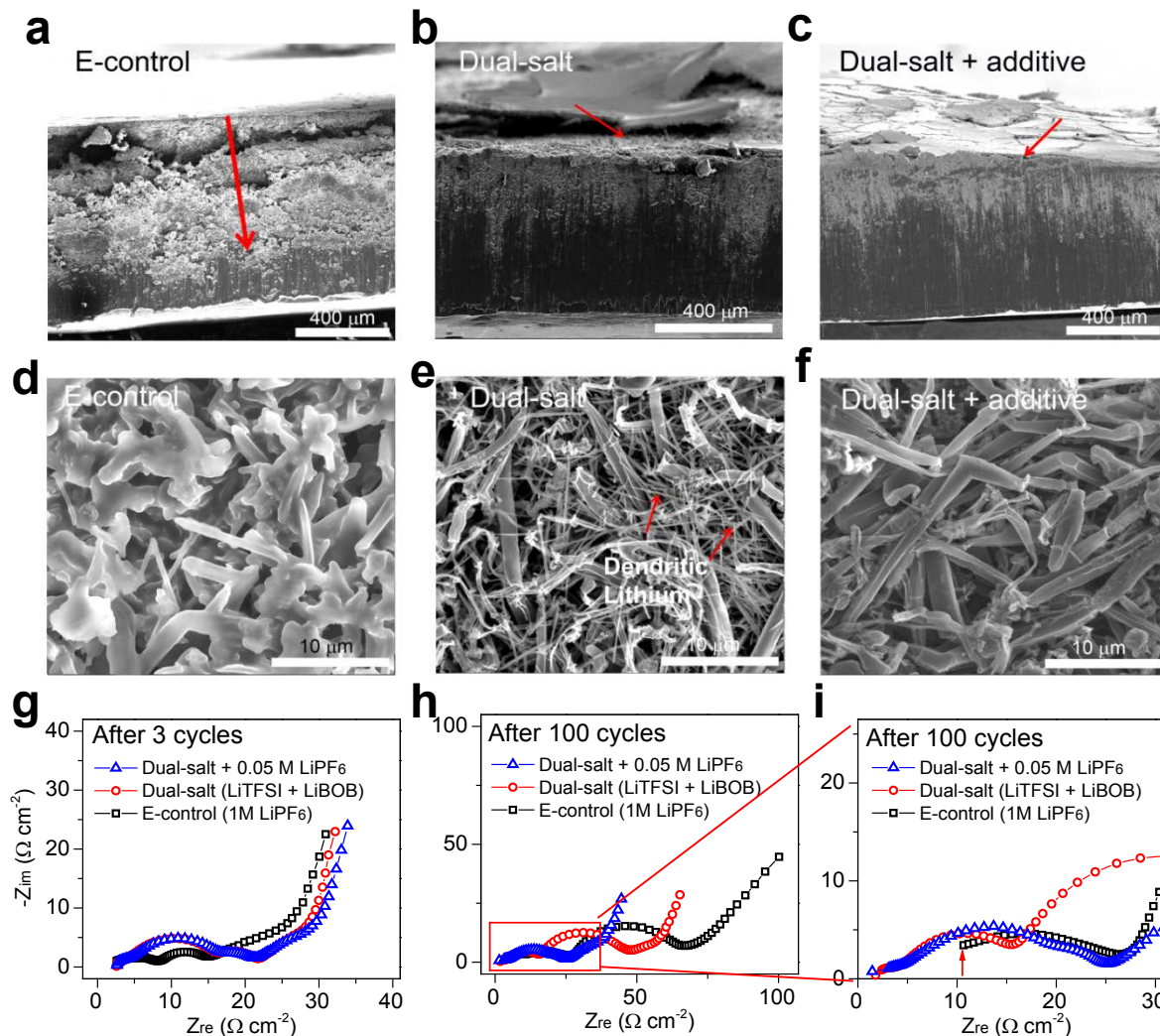
## Long-term cycling and rate performances of Li||NMC batteries with different electrolytes



- ✓ LiTFSI-LiBOB electrolytes allow the Li||NMC cells to show much better cycling performance than LiPF<sub>6</sub> electrolyte at fast charging/discharging current density (1.75 mA cm<sup>-2</sup>) and room temperature (30°C)/elevated temperature (60°C).
- ✓ **LiPF<sub>6</sub> additive at optimum (0.05 M) further improves the charge/discharge rate capability of the dual-salt electrolyte.**

# Technical Accomplishments

## Characterization of morphological behaviour and interfacial evolution of Li metal anodes

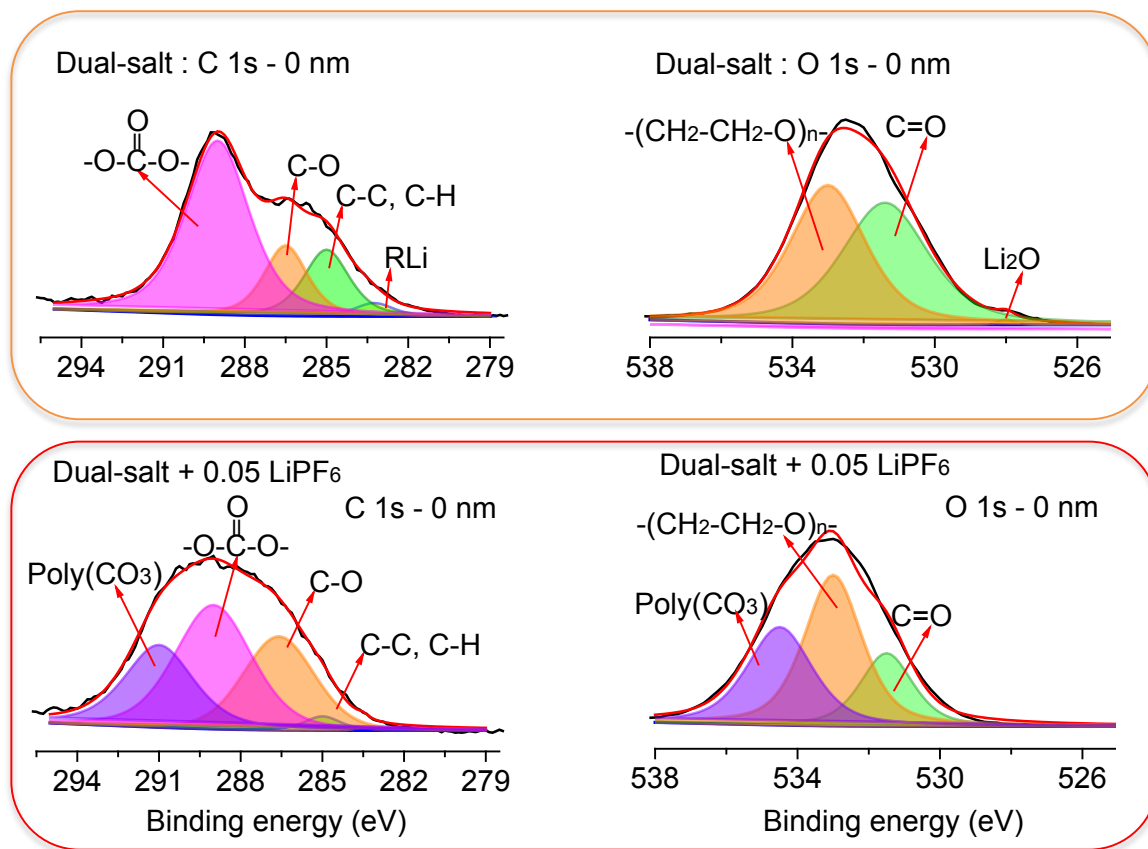


- ✓ LiPF<sub>6</sub> additive reduces the corrosion of Li metal, leads to the formation of uniform fibrous Li wires, and mitigates the growth of chaotic Li dendrites.
- ✓ LiPF<sub>6</sub> additive induces the generation of a dense, compact and highly conductive SEI layer on Li metal anode.



# Technical Accomplishments

## Compositions of the SEI layers formed on cycled Li metal anodes



- LiPF<sub>6</sub> additive induces the generation of an SEI layer enriched with polycarbonate constituents.
- Polycarbonates can keep good adhesion of SEI layer together and onto Li anode to well protect Li metal.

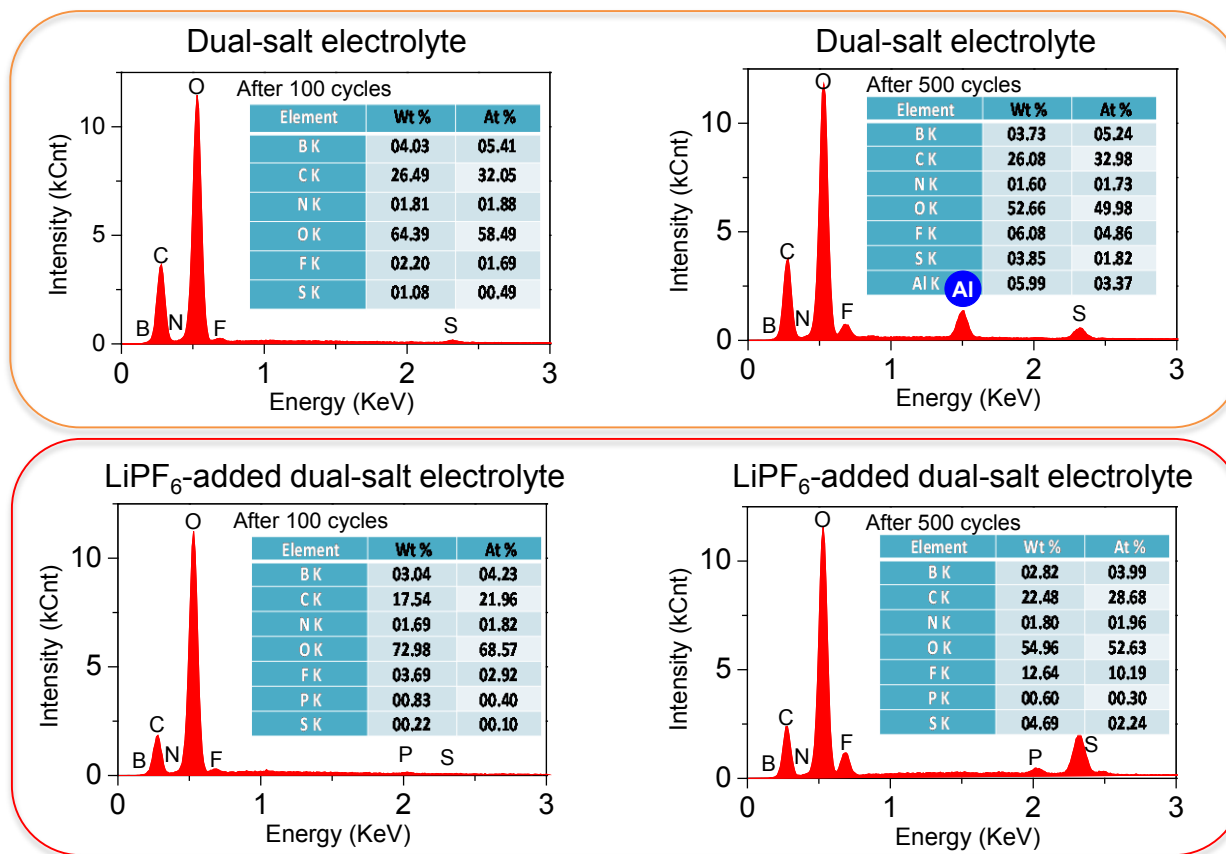


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# Technical Accomplishments

## Evolution of compositions in SEI layers on cycled Li metal anodes after long cycling of Li||NMC cells



- ✓ LiPF<sub>6</sub> additive mitigates the consumption of electrolyte for SEI formation.
- ✓ LiPF<sub>6</sub> additive is also beneficial for stabilizing Al current collector.

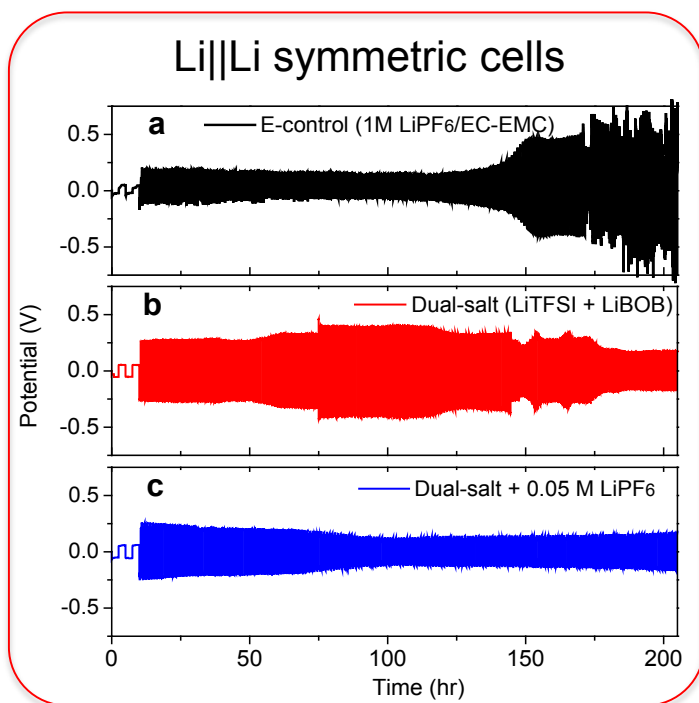


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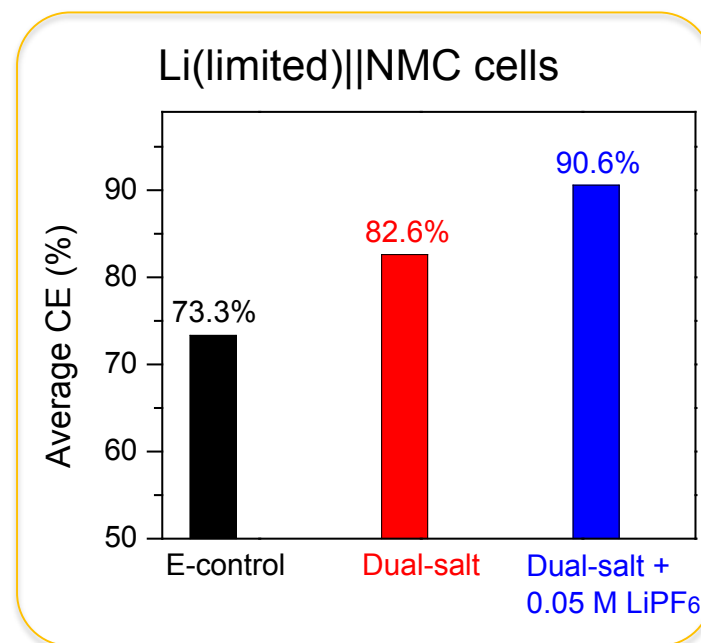
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# Technical Accomplishments

## Electrochemical analysis on effect of $\text{LiPF}_6$ additive on stability of LiTFSI-LiBOB dual-salt electrolyte



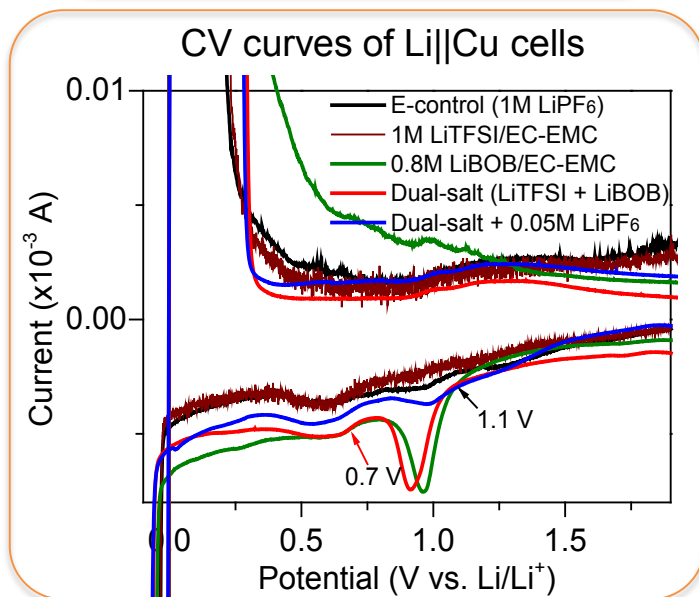
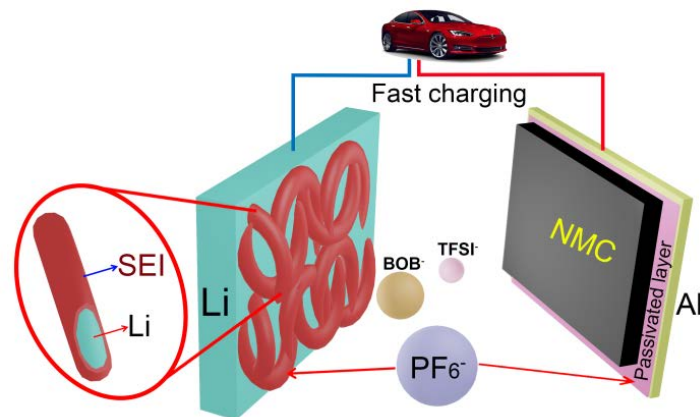
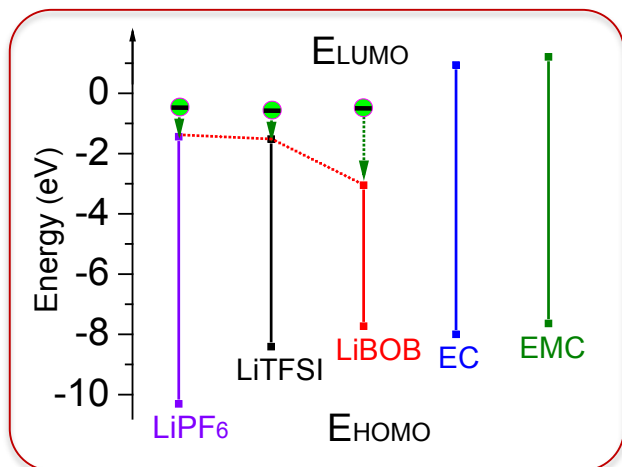
- $\text{LiPF}_6$  additive improves the stability and conductivity of SEI layer on Li meal.



- ✓  $\text{LiPF}_6$  additive improves the average CE of Li metal to 90.6%.
- ❖ However, the Li CE is still not high enough and the electrolyte needs further development.

# Technical Accomplishments

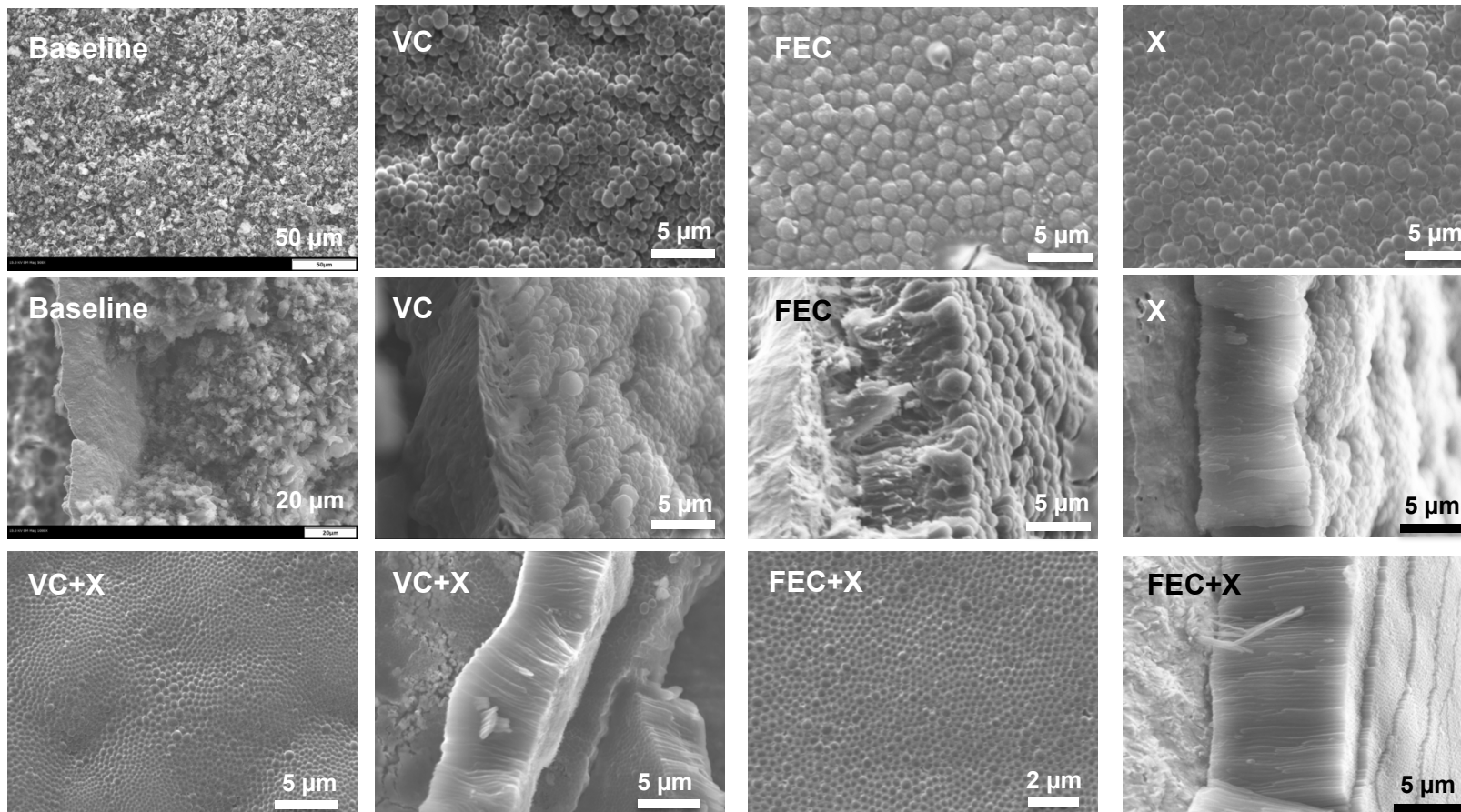
## Schematic illustration of $\text{LiPF}_6$ additive improving $\text{Li}||\text{NMC}$ cell performances



- LiBOB first decomposes at both Li anode and NMC cathode to form SEI films.
- ✓  **$\text{LiPF}_6$  additive mitigates the reductions of Li salts, especially LiBOB.**
- ✓  **$\text{LiPF}_6$  additive induces the generation of a robust and conductive SEI layer enriched with polycarbonate constituents.**
- ✓  **$\text{LiPF}_6$  additive also stabilizes Al current collector.**

# Technical Accomplishments

## Effect of additives on morphologies of deposited Li metal



- Li deposited on Cu foil at  $0.1 \text{ mA cm}^{-2}$  for 15 h
- Baseline electrolyte: 1 M  $\text{LiPF}_6$  in PC
- ✓ **VC+X and FEC+X additive mixtures lead to more smooth, uniform and dense nanorod Li metal deposition.**



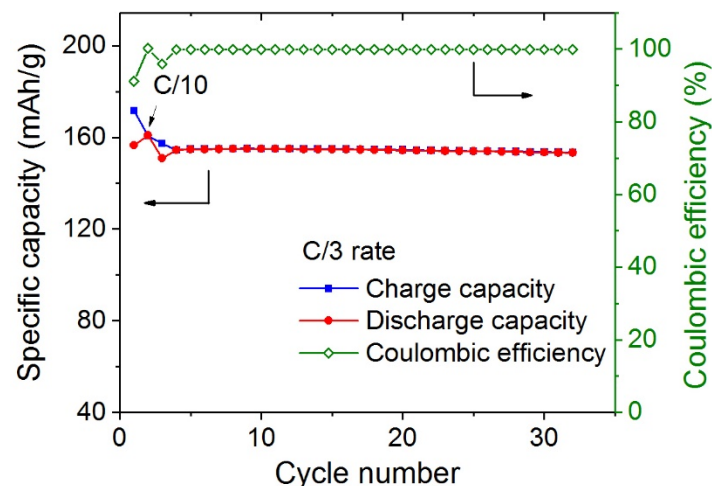
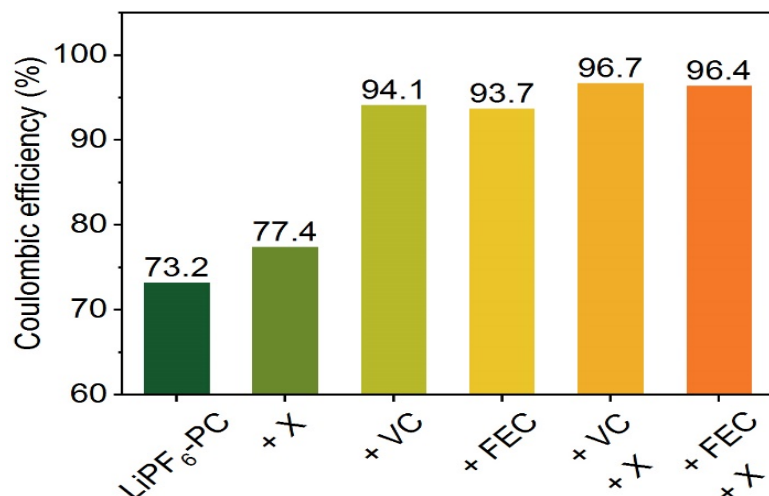
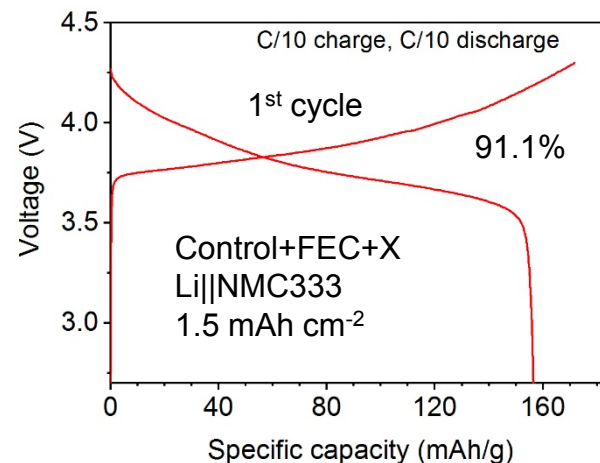
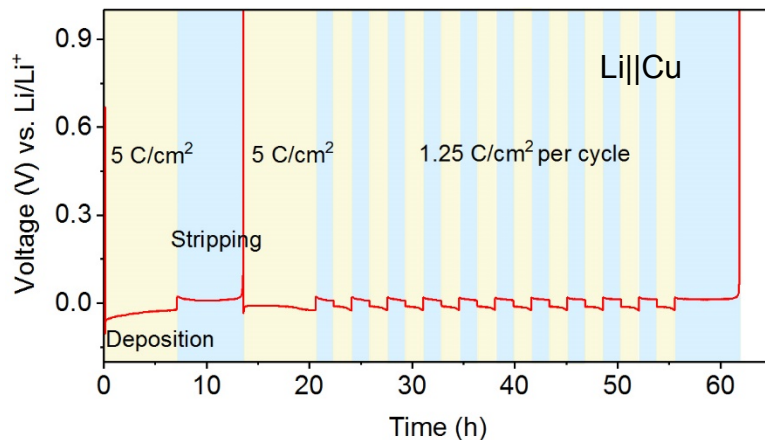
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# Technical Accomplishments

## Effect of additives on Li CE and cycling performance



✓ Additives especially additive mixtures greatly increase Li CE.

➤ Li||NMC333 cell has demonstrated a stable cycling with an efficiency of 99.9% (Testing is continued).



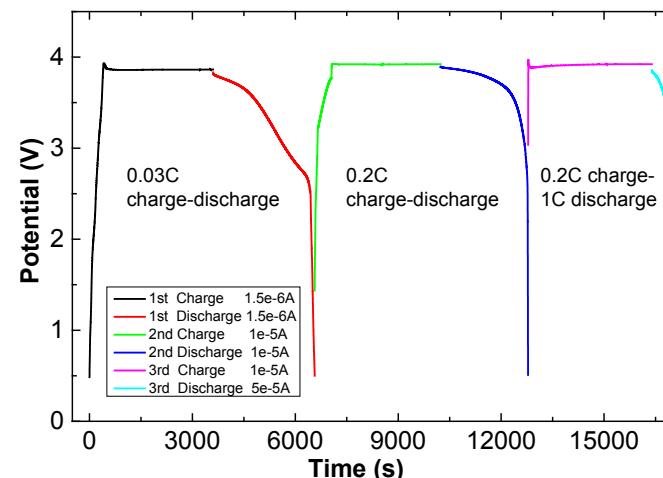
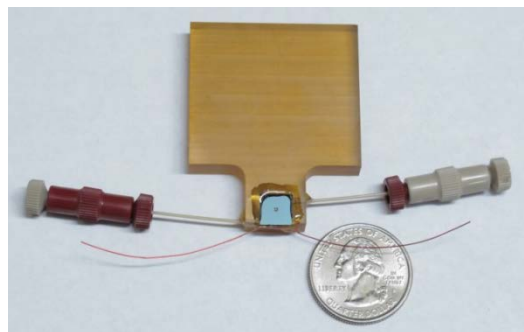
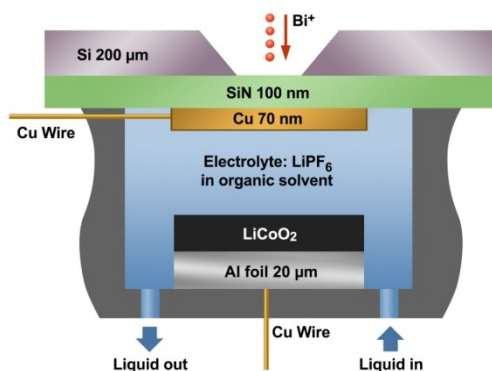
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# Technical Accomplishments

## In-situ ToF-SIMS analysis on Li anode surface during fast and slow discharge rates

- Electrochemical cell for ToF-SIMS measurement
  - Cu||LiCoO<sub>2</sub> with the electrolyte of 1.0 M LiPF<sub>6</sub> in EC-EMC
  - Li was first deposited on Cu substrate by charging the cell at a slow rate.
  - Then the cell was discharged at fast and slow rates.



- Analyzed SEI components on Li anodes during fast and slow discharge rates.
- Difference in Li<sup>+</sup>-content in SEI on Li anode from fast and slow discharge rates (1C vs. C/5) is small → A concentrated electrolyte layer was not observed.



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# Responses to Previous Year Reviewers' Comments

- The project was not reviewed in 2016.



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# Collaboration and Coordination with Other Institutions

## Partners:

- Argonne National Laboratory: Provided coated NMC cathode sheets for testing.
- Army Research Laboratory: Conducted DSC and ionic conductivity measurements.



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# Remaining Challenges and Barriers

- Low Coulombic efficiency of Li metal anode during cycling.
- Cycling stability of Li metal batteries with high loading cathodes.
- Cycling stability of Li metal batteries with limited electrolyte amount.
- Li metal dimension or volume change during charging and discharging cycles.



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# Future Work - FY2017/18

- Continue to evaluate electrolytes in 4-V Li-metal batteries with high cathode loading and at relatively high current density cycling.
- Continue to develop electrolytes with Li Coulombic efficiency over 99% and stable at 4.5 V.
- Develop ionic conductive protection layer on Li metal anode to reduce parasitic reactions between Li metal and electrolytes.

Any proposed future work is subject to change based on funding levels.



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# Summary

- ✓ Developed  $\text{LiPF}_6$  as an effective additive in LiTFSI-LiBOB dual-salt electrolytes to achieve fast chargeability and long-term cycling stability of Li metal batteries.
  - ✓ Dense and compact fibrous Li deposition is obtained.
  - ✓ Highly conductive SEI is formed.
  - ✓ Polycarbonate species are generated in SEI to keep good adhesion of SEI layer onto Li metal.
  - ✓ Good protection of Li metal anode is achieved.
  - ❖ Li CE is improved, but it needs further improvement.
- ✓ Developed additive mixtures (VC+X and FEC+X) to significantly improve morphologies of deposited Li metal and Li CE.
  - ✓ Smooth, uniform and dense nanorod Li metal deposition.
  - ✓ Increased Li CE from 73% to near 97%.
- Analyzed SEI components on Li anodes during fast and slow discharge rates.
  - A concentrated electrolyte layer was not observed.



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# Acknowledgments

- Support from the DOE Vehicle Technologies Office Advanced Battery Materials Research program is greatly appreciated.
- Team Members:  
Jianming Zheng, Shuhong Jiao, Xiaodi Ren, Donghai Mei,  
Mark H. Engelhard, Xing Li, Zihua Zhu, Xiaofei Yu



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# ***Technical Backup Slides***

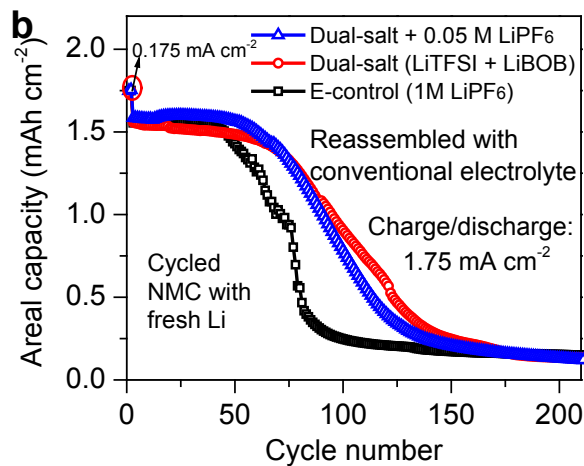
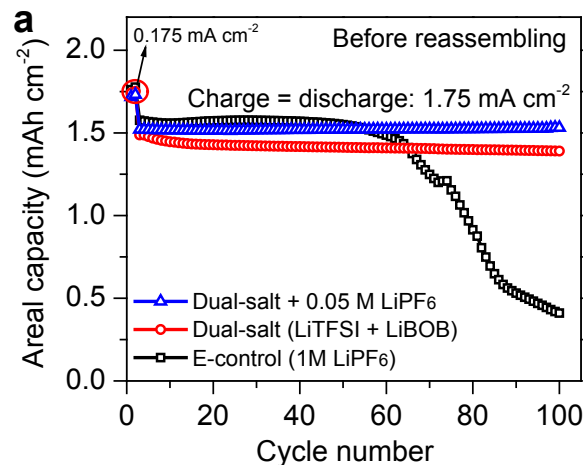
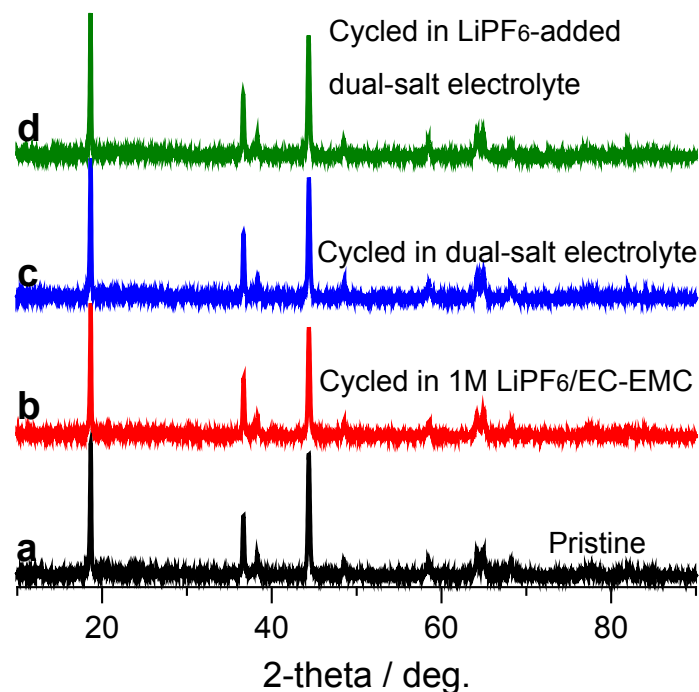


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# Technical Accomplishments

## Analysis on cycled NMC cathodes and cycling performance of reassembled Li||NMC cells



- LiPF<sub>6</sub> additive shows limited effect on the NMC cathode materials, especially during early stage of cycling.
- LiPF<sub>6</sub> additive should mainly improve the stability of Li metal anode.



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# Technical Accomplishments

## Impedance data of Li||NMC cells using different electrolytes after 100 cycles

	3 <sup>rd</sup> cycle resistance (ohm cm <sup>-2</sup> )		100 <sup>th</sup> cycle resistance (ohm cm <sup>-2</sup> )	
	$R_e$	$R_{\text{interfacial}}$	$R_e$	$R_{\text{interfacial}}$
E-control	2.0	11.7	9.0	49.2
Dual salt	2.2	17.1	2.2	40.8
Dual salt + 0.05 M LiPF <sub>6</sub>	2.2	16.1	2.2	20.1

- The intercept of the high frequency response with the real axis is an indication of the electrolyte resistance ( $R_e$ ).
- The intermediate-to-high-frequency semicircles are related to the charge transfer resistance ( $R_{ct}$ ) in the electrode/electrolyte interface and the passivation surface film—the so-called SEI layer resistance ( $R_{sf}$ ).
- The total of  $R_{ct}$  and  $R_{sf}$  is considered the interfacial resistance ( $R_{\text{interfacial}}$ ).
- The low-frequency tail is associated with the Li<sup>+</sup> ion diffusion process in the solid electrode.
- **LiPF<sub>6</sub>-added LiTFSI-LiBOB electrolyte results in low resistances after long cycling.**



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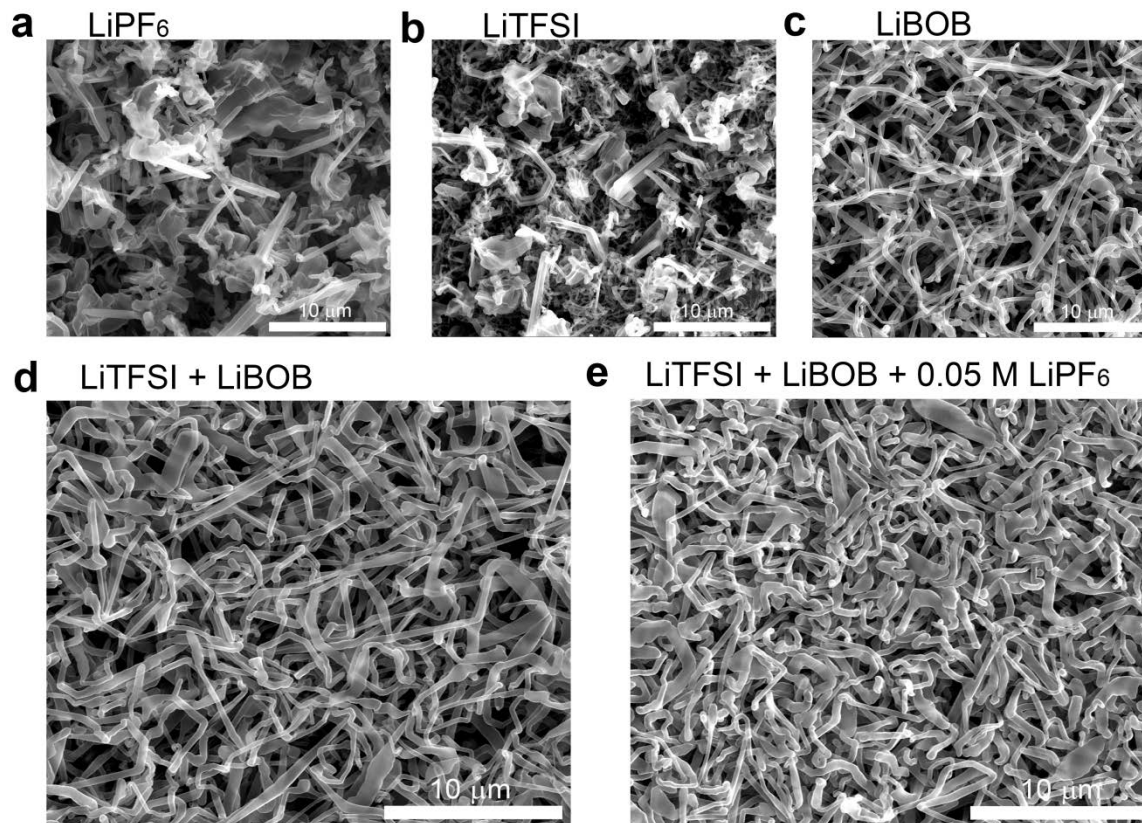
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# Technical Accomplishments

## Morphologies of deposited Li metal in electrolytes containing different salts and additive

- Li||Cu cells.
- Li deposition on Cu at 1.75 mA cm<sup>-2</sup> for 1 h.
- EC-EMC solvent.
- Total 1.0 M salt concentration.



- LiPF<sub>6</sub> and LiTFSI electrolytes lead to chaotic and dendritic Li growth.
- ✓ LiBOB based electrolytes result in fibrous and uniform Li growth.
- ✓ LiPF<sub>6</sub> additive in dual-salt electrolyte enables dense and compact Li growth.

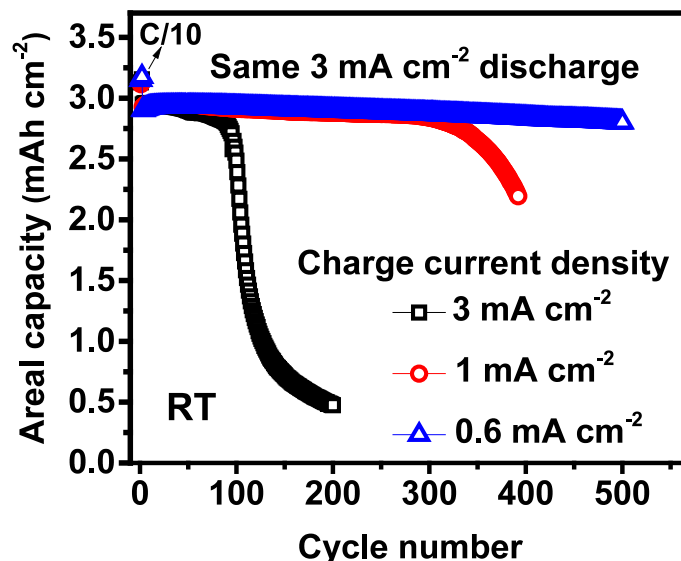


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# Technical Accomplishments

## Long-term cycling performance of Li||NMC cells with a high areal loading NMC cathode at 30°C



- Li||NMC cells with a high areal loading NMC cathode of 3.0 mAh cm<sup>-2</sup>.
- Optimal LiPF<sub>6</sub>-containing LiTFSI-LiBOB electrolyte.
- 1C charge → 100 stable cycles.
- C/3 charge → 300 stable cycles.
- C/5 charge → at least 500 stable cycles.
- ✓ **The optimized electrolyte enables good cyclability of Li metal batteries with a high loading cathode.**

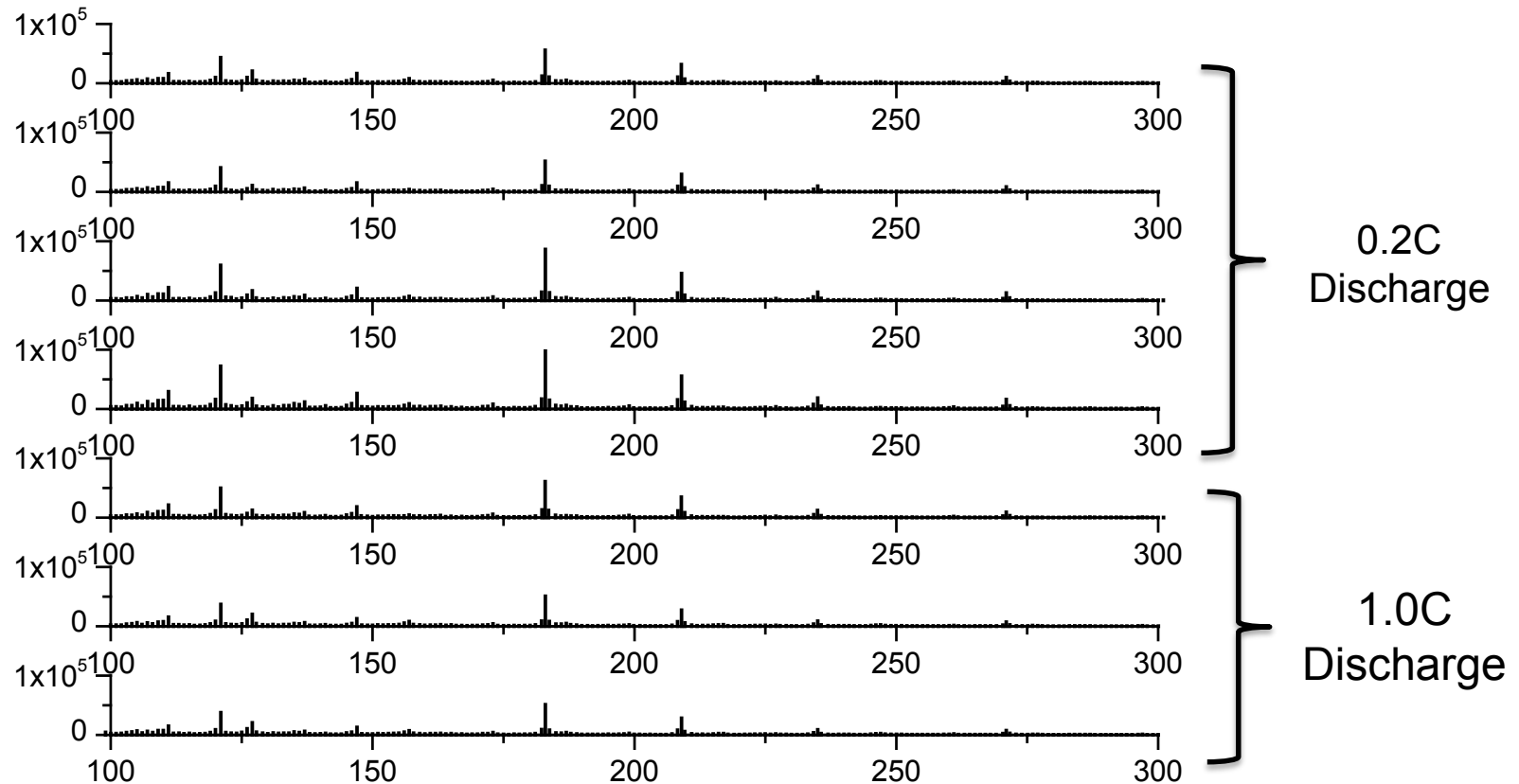


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# Technical Accomplishments

## ToF-SIMS spectra of the component signals during slow and fast discharge rates



- The spectra of the electrolyte signals (including EC+Li, 2EC+Li, and 3EC+Li) do not show any significant difference between the two discharge rates.



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